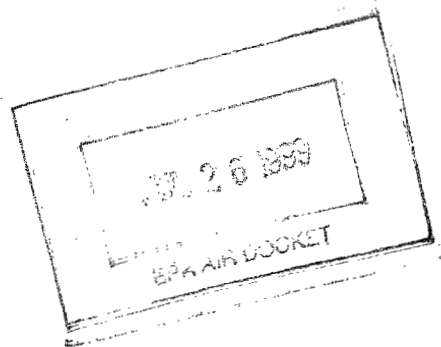




**ALPHA-GAMMA**  
TECHNOLOGIES, INC.

August 2, 1996

Mr. Terry Harrison  
U.S. Environmental Protection Agency  
Emissions Measurement Center  
MD-19  
Research Triangle Park, NC 27711



Dear Terry:

Based on Sims Roy conversation with you regarding CARB Method 430, I am forwarding the following documents for your review and reference:

- 1) letter submitted by James McCarthy of GRI to Sims Roy on July 19, 1996;
- 2) copy of the material referenced by Mr. McCarthy in his July 19th letter (pages 3-6 and 3-7 of GRI's Topical Report, "Measurement of Air Toxic Emissions from Natural Gas-Fired Internal Combustion Engines at Natural Gas Transmission and Storage Facilities," Report No. GRI-96/0009.1);
- 3) copy of the document "Measurement of Gaseous Formaldehyde, Phenol and Methanol Emissions by FTIR Spectroscopy" posted on EPA's TTN Bulletin Board; and
- 4) an internal memorandum submitted to the project files summarizing the difference between CARB Method 430 and GRI's FTIR method as referenced in the GRI's Topical Report "Fourier Transform Infrared (FTIR) Method Validation at a Natural Gas-Fired Internal Combustion Engine," Report No. GRI-95/0271.

If you have any questions or require any additional information, please do not hesitate to contact me at 954-0033 or Sims Roy at 541-5263.

Sincerely,

Brahim Richani, Ph.D.  
Mechanical Engineer

Enclosures (4)

cc: Sims Roy, US EPA, MD-13  
Amanda Agnew, US EPA, MD-13

Gas Research Institute  
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Chicago, Illinois 60631-3562  
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FAX: 312/399-8170



July 19, 1996

Mr. Sims L. Roy, Jr., P.E.  
Senior Environmental Engineer  
Environmental Protection Agency  
Office of Air Quality Planning and Standards, MD-13  
Research Triangle Park, NC 27711

SUBJECT: Combustion Turbine (CT) Definitions and Test Methods

Dear Sims:

Thank you for providing GRI the opportunity to comment on the draft definitions and test methods for combustion turbines and reciprocating internal combustion engines which were distributed on June 19, 1996. In response to your request, GRI is preparing comments on the definitions and test methods. In order to allow adequate time to prepare comments for submission, we request an additional 30 days (until August 19, 1996) to provide comments.

GRI is especially interested in commenting on the test methods used to measure formaldehyde emissions from natural gas turbines and internal combustion (IC) engines. As you will recall, GRI developed an FTIR method that was subsequently approved by EPA for measurement of emissions from natural gas-fired combustion sources. While developing this method, GRI noted some irregularities in the CARB 430 method performance for measurement of formaldehyde emissions from IC engines. The June 19 draft raises the question of CARB 430 performance within the context of turbines. However, the GRI HAPs testing program has focused largely on IC engines and the CARB 430 irregularities witnessed by GRI occurred during testing of IC engines. During GRI's limited testing on turbines, no CARB 430 irregularities were noted.

The CARB 430 performance is discussed on pages 3-6 and 3-7 of the GRI Topical Report, "Measurement of Air Toxic Emissions from Natural Gas-Fired Internal Combustion Engines at Natural Gas Transmission and Storage Facilities," which was provided to you on May 2, 1996. In that report, GRI indicates that differences between the FTIR method and the CARB 430 method were observed in some of the engine test results:

In several cases where aldehydes were measured above detection limits using the FTIR, they were not observed in the analysis of the samples performed by [CARB 430].

Mr. Sims Roy  
July 19, 1996  
page 2


The report suggests that the cause of these differences may be due to nitrogen dioxide (NO<sub>2</sub>) interference with the CARB 430 reagent, 2,4-dinitrophenylhydrazine (DNPH). Recent results from two other aldehyde research programs also suggest that potential interference for the DNPH measurement methods may be caused by NO<sub>2</sub> present in the exhaust gas:

1. Scull, N., C. Kim, and D.E. Foster. *Comparison of Unburned Fuel and Aldehyde Emissions from a Methanol-Fueled Stratified Charge and Homogeneous Charge Engine*. Society of Automotive Engineers, Paper 861543.
2. Karst, U., A. H. J. Cromping, N. Bindings, U. Witting, and K. Cammann. "Determination of Aldehydes, Ketones, and Nitrogen Oxides in Automobile Exhaust." *American Environmental Laboratory*. Vol. 7, No. 2, pp. 32-33, March 1995.

Since this GRI Topical Report was released, GRI has done some additional work to address the CARB 430 issue. We plan to provide additional information about the GRI research in our response to your June 19 distribution. Also, this data will be included in a GRI Topical Report scheduled for release in the first quarter of 1997.

EPA will need to address the CARB 430 performance issue as the Agency collects the emissions data required for the MACT standard development. Thank you for considering our request for a 30-day extension of the comment period. We look forward to working with EPA under the Industrial Combustion Coordinated Rulemaking (ICCR).

Sincerely,



James McCarthy  
Program Team Leader, Air Quality

## **Topical Report**

# Measurement of Air Toxic Emissions from Natural Gas-Fired Internal Combustion Engines at Natural Gas Transmission and Storage Facilities

## Volume I

*Prepared by:*  
*Gunseli Sagun Shareef*  
*Kathy R. Ferry*  
*Mahesh Gundappa*  
*Chad A. Leatherwood*  
*Larry D. Ogle*  
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*Radian Corporation*

### 3.1.1 Exhaust Gas Flow Rate

Exhaust gas flow rates were estimated using EPA Methods 2 and 19. Method 2 uses pitot tube velocity measurements and temperature data to calculate volumetric flow rate, while Method 19 employs a factor based on combustion stoichiometry that relates the amount of fuel burned to the exhaust gas flow rate. Accuracy of Method 2 data can be affected by the pulsations caused by the noncontinuous flow from each piston, whereas the accuracy of Method 19-based flow rates is dependent on reliable fuel flow rate data. For most of the test runs, emission rates were determined using Method 19, except where accurate fuel flow rate data were unavailable.

### 3.1.2 Procedures

FTIR measurements were conducted according to procedures described in a protocol document prepared for this field measurement program.<sup>8</sup> Results from FTIR validation testing performed under a separate effort have been reviewed by EPA and the FTIR method has been approved as a valid method for measuring concentrations of formaldehyde, acetaldehyde, acrolein, NO<sub>x</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O in engine exhaust. A copy of the EPA approval letter is included as an attachment to this volume.

Measurements for other target compounds were conducted according to established procedures specified in the state and federal methods (see Appendix B for detailed description of the methods).

As the data collection effort was refined based on review of information from initial campaigns, some of the measurements were discontinued. For example, metal emission measurements were conducted only during Campaign 1. Similarly, measurement of PM<sub>10</sub> emissions (particulate and condensable) was not conducted after Campaign 4.

### 3.1.3 CARB Method 430 Formaldehyde Measurements

As indicated above, measurements of formaldehyde and other aldehydes were conducted via the FTIR method and CARB Method 430 during all campaigns. In some campaigns, SW-846 Method 0011 was also used to measure aldehydes. Differences

between the FTIR method and the two manual methods were observed in some of the test results. Both manual methods are based on quantifying the amount of derivatization occurring between the aldehydes and 2,4-dinitrophenylhydrazine (DNPH) in impinger solutions. In several cases where aldehydes were measured above detection limits using the FTIR, they were not observed in the analysis of the samples performed by manual methods. In several of these cases, trace amounts of the aldehydes were found in the field blanks. Impinger solutions were observed to be clear instead of the orange color typically associated with DNPH, indicating potential cross-reactions that consumed the reagent.

Recent results reported in the literature indicate that potential interferences for the DNPH measurement methods may be caused by nitrogen dioxide ( $\text{NO}_2$ ) present in the exhaust gas.<sup>2,23</sup> GRI has conducted laboratory tests investigating the potential impacts of  $\text{NO}_2$  on measurement of formaldehyde using DNPH-based methods. Results of this study are documented in the gas plant report.<sup>3</sup>

#### 3.1.4 Measurement System Description (Extractive)

A schematic of the exhaust gas sample extraction and analysis system used during the field measurements is shown in Figure 3-1. Samples were extracted from the engine/turbine stacks using a stainless steel filter and probe assembly. Sample gas was transferred through a heat-traced line to the mobile laboratory using a heated-head pump, followed by delivery to the insulated sample manifold for further distribution. Sample gas was then conditioned, if required, by passing it through a series of chillers. Conditioned gas was delivered to the  $\text{NO}_x$ , CO,  $\text{CO}_2$ , and  $\text{O}_2$  analyzers, while unconditioned gas was delivered to the FTIR, GC, and THC analyzers. A listing of the instruments used during the field measurements is shown in Table 3-3.

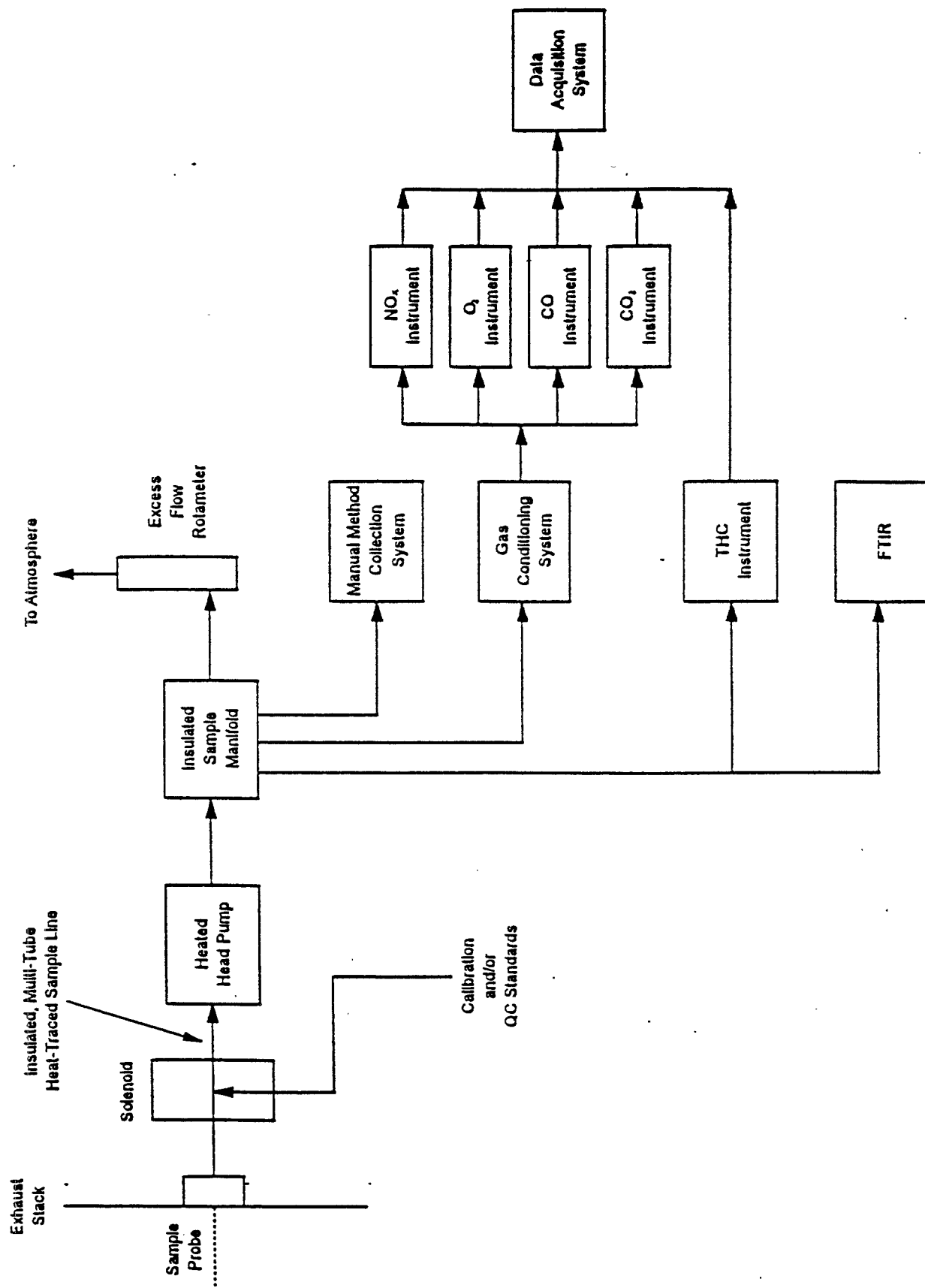


Figure 3-1, Sample Extraction System Schematic

## MEASUREMENT OF GASEOUS FORMALDEHYDE, PHENOL AND METHANOL EMISSIONS BY FTIR SPECTROSCOPY

### Introduction

This method should not be attempted by persons untrained in the operation of FTIR instrumentation nor by persons unfamiliar with source sampling. This document describes the sampling procedures to be employed when using FTIR spectrometry for the determination of gaseous formaldehyde, phenol and methanol concentrations from manufacturing processes using phenolic resins. A procedure for analyte spiking is also included for purposes of quality assurance. The analytical procedures to be used for FTIR emission measurements are fully described in the *EPA Draft Version S8 [9-30-94] Protocol for the use of Extractive Fourier Transform Infrared Spectrometry in Analyses of Gaseous Emissions From Stationary Industrial Sources (FTIR Protocol)*.

#### 1.0 Scope and Application

1.1 Analytes. This method applies to the measurement of formaldehyde, phenol, and methanol. Their CAS numbers are listed below.

Formaldehyde	50-00-0
Phenol	108-95-2
Methanol	1455-13-6

1.2 Applicability. This method is applicable for the determination of formaldehyde, phenol and methanol concentrations in controlled and uncontrolled emissions from manufacturing processes using phenolic resins. The method applies to either continuous monitoring (flow-through analysis) or grab sampling (batch analysis). The compounds are measured using the mid-infrared region (about 400 to 4000  $\text{cm}^{-1}$  or 25 to 2.5  $\mu\text{m}$ ) for analysis.

1.3 Method Range and Sensitivity. The analytical range is determined by the instrumental design and other components of the gas stream. For practical purposes there is no upper limit to the range. Theoretical detection limits depend, in part, on (1) the absorption coefficient of the compound in the analytical frequency region, (2) the spectral resolution, (3) interferometer sampling time, (4) detector sensitivity and response, and (5) absorption pathlength. Factors 2, 3, 4, and 5 can be chosen by the analyst. Before testing, the analyst should determine acceptable lower detection limits ( $\text{DL}_t$ ) and acceptable analytical uncertainty ( $\text{AU}_t$ ) for each compound. The instrumental parameters are then chosen to meet these requirements. Procedures for determining suitability of the system configuration are found in Reference 1, Section 4.11. The practical detection limit is usually higher than the theoretical value, and depends on (1) moisture content of the flue gas, (2) presence of unexpected interferants, and (3) losses in the sampling system. In general, a 22 meter pathlength cell, used with a suitable sampling system, can achieve practical detection limits of roughly 2 ppm for these three compounds at a percent moisture level of roughly 15%.

1.4 Data Quality Objectives. Data quality is determined, in part, by measurements of the root mean square deviation (RMSD) noise levels in absorbance spectra. Appendix D of Reference 1 provides a complete discussion relationship between noise levels and the quantities  $\text{DL}_t$  and  $\text{AU}_t$ .

#### 2.0 Summary of Method

2.1 Principle. All molecules are composed of chemical bonds that vibrate. Molecules undergo transitions from lower to higher vibrational states by absorbing infrared energy. The number of atoms in a molecule (N) determines the number of fundamental (or independent) vibrational motions ( $3N-6$  for non-linear molecules, and  $3N-5$  for linear molecules). Absorbance of infrared radiation (energy) occurs when a molecule undergoes a transition from a lower energy state to a higher state for a particular vibrational motion (or combination of vibrational motions). The frequency of the absorbed energy is characteristic of the molecule and the molecular motion. Molecules also undergo rotational transitions by absorbing energies in the far-infrared or microwave regions. Absorbances for rotational transitions are superimposed on the vibrational absorbencies to give a characteristic shape to each vibrational absorbance "band." The frequencies of absorbance and the band



shapes are used to identify compounds from their infrared spectra. Most molecules absorb infrared energy in more than one frequency region to produce an infrared spectrum. This results in a characteristic pattern of bands (a "fingerprint") which is unique for each molecule. The infrared spectrum of a molecule depends on its structure (bond lengths, bond angles, bond strengths, and atomic masses). Even small differences in structure give rise to significant differences in the spectrum that help to distinguish molecules based on their infrared spectra alone.

The intensities of infrared absorbance bands depends on the concentration of the absorbing compound in the sample. Within constraints, the relationship between absorbance and sample concentration is linear. Spectra of laboratory standards are used to measure the concentrations of detected species in spectra of flue gas samples.

2.2 Sampling and Analysis. Flue gas is continuously extracted from the source, and a portion of the gas is conveyed to the FTIR analytical components. An infrared spectrum of the flue gas is obtained by passing an infrared beam through the gas sample contained in a gas cell. Absorbance band intensities are related to sample concentrations by Beer's Law

$$A = abc$$

(1)

where

A = absorbance at a given frequency

a = absorption coefficient

b = path length of the cell

c = concentration of the compound in the sample

Identification and quantification are performed by comparing sample spectra to "reference spectra" of compounds, many of which are available in a permanent soft copy from the EPA spectral library. The spectra of formaldehyde, phenol and methanol have been prepared under carefully controlled laboratory conditions, at a series of known (measured) concentrations.

2.3 Operator Requirements. The analyst must have some rudimentary knowledge of spectral patterns to determine absorption path length or to determine if sample dilution is necessary. The analyst should also understand FTIR instrument operation well enough to choose instrument settings that are consistent with the objectives of the analysis.

### 3.0 Definitions

For a full list of definitions, see Reference 1, Appendix A.

### 4.0 Interferences

This method will not measure formaldehyde, phenol or methanol under conditions: (1) which promote polymerization of the formaldehyde, (2) which promote condensation of the gas stream in either the sampling system or the instrumentation, and (3) where the moisture content of the gas stream is so high relative to the analyte concentrations that severe spectral interference results from the water vapor absorbance bands.

4.1 Analytical (or Spectral) Interferences. Analytical interferences are those that specifically inhibit FTIR analysis, and can be divided into background interferences and spectral interferences.

4.1.1 Background interferences. These are caused by changes in the background single beam spectrum that occur during the sampling period. Such changes may be caused by: (1) contamination deposits on reflective surfaces or transmitting windows, (2) changes in detector sensitivity, or (3) increase or decrease in the output of the infrared source.

4.1.2 Spectral interferences. These are caused by the presence of species in the gas matrix giving absorption in overlapping spectral regions used for analyte quantification. Water vapor and CO<sub>2</sub> can present significant spectral interference for FTIR gas analysis. The degree of interference depends on the concentration of the interferant, sensitivity of the FTIR instrumentation, concentration of the analyte, and spectral profile of the analyte.

4.2 Sampling System Interferences. A sampling system interferant is a factor that inhibits an analyte from reaching the analytical instrumentation. Condensed water vapor is a strong sampling system interferant for water soluble compounds such as formaldehyde, phenol and methanol. Cold spots in the sampling system can cause regions of condensation where water soluble species will be removed from the gas stream. The extent of sampling system biases in FTIR analysis for formaldehyde, phenol and methanol depend on

concentrations of potential interferants, moisture content of the gas stream, temperature of the gas stream, temperature of sampling system components, and reactivity of formaldehyde, phenol and methanol with other species in the gas stream.

4.2.1 Analyte spiking. Performing analyte spiking with formaldehyde, phenol, and methanol demonstrates the integrity of the sampling system for measurement of these water soluble and otherwise unstable species.

## 5.0 Safety

This method may involve sampling at locations having high positive or negative pressures, or high concentrations of hazardous or toxic pollutants, and can not address all safety problems encountered under these diverse sampling conditions. It is the responsibility of the tester(s) to ensure proper safety and health practices, and to determine the applicability of regulatory limitations before performing this test method. Because formaldehyde is a suspect carcinogen, it is advisable to limit exposure to this compound.

## 6.0 Equipment and Supplies

6.1 FTIR Spectrometer and Detector. An FTIR Spectrometer system having the capability of measuring formaldehyde, phenol and methanol to the predetermined minimum detectable level is required. The system must include a personal computer with compatible software that provides real-time updates of the spectral profile during sample collection and spectral collection.

6.2 Pump. Capable of evacuating the FTIR cell volume within two minutes (for grab sample type of analysis), or delivering a constant and measurable flow rate through the cell for continuous monitoring.

6.3 Mass Flow Meters. To accurately measure analyte spike flow rate, having a calibrated range from 0-2 L/min ( $\pm 5\%$ ) should be sufficient.

6.4 Teflon Tubing. Diameter and length suitable to connect cylinder regulators.

6.5 Stainless Steel Tubing. 316, appropriate length and diameter for heated connections.

6.6 Gas Regulators. Appropriate for individual gas cylinders.

6.7 Pressure Gauge. Capable of measuring pressure from 0 to 1000 Torr ( $\pm 5\%$ ).

6.8 Sampling Probe. Glass, stainless steel or other appropriate material of sufficient length and physical integrity to sustain heating, prevent adsorption of analytes and to reach gas sampling point.

6.9 Sampling Line. Heated (temperatures sufficient to prevent sample condensation) stainless steel, Teflon, or other inert material that prevents adsorption of analytes and transports effluent to analytical instrumentation.

6.10 Particulate Filters. A filter of glass wool may be inserted at the probe tip (for removal of large particulate matter). A filter (Balston™ or equivalent) rated at 1 micron for particulate removal is necessary, and should be placed immediately after the heated probe.

6.11 Calibration/Analyte Spike Assembly. A three way valve assembly (or equivalent) to introduce formaldehyde and phenol spikes into the sampling system at the outlet of the probe before the particulate filter(Balston™).

6.12 Sample Pump. A leak-free pump (KNF™ or equivalent) capable of pulling sample through entire sampling system at a rate which prevents analyte losses and minimizes analyzer response time. The pump may be placed either before the FTIR or after. In the former case, the pump must be heated or fabricated from materials non-reactive to the formaldehyde and phenol. It is desirable to have a by-pass valve on the pump. The sampling system and FTIR cell pump should obtain 6-10 sample spectra in a one-hour period.

6.12 Pressure Measurement Gauge. For measurement of gas sample cell pressure (Baratron™ or equivalent)

6.13 Barometer. For measurement of barometric pressure.

6.14 Gas Sample Manifold. A manifold that diverts part of the sample stream to the analyzer, and the rest to the by-pass discharge vent or other analytical instrumentation.

6.15 Calibration Transfer Standard. Gas cylinder that meets requirements described in the *FTIR Protocol*. CTS can also be used for verifying dilution ratio during spiking procedures if it is not already present in the source matrix. Ethylene has been used effectively as a CTS gas (Reference 4).

6.16 Nitrogen.

## 7.0 Reagents and Standards

7.1 Formaldehyde and Phenol. Formaldehyde and phenol are reactive compounds that are difficult

to obtain in gas cylinders under stable conditions. Formaldehyde is commercially available at a concentration of approximately 5 ppm in a balance of nitrogen, and phenol is currently not available. Preparation of gas standards for these compounds may be performed by generation of the gas from the reagent grade chemicals. Paraformaldehyde and phenol solids may be purchased from Aldrich. Alternately, liquid standards may be used if their purity is certified. Gas standards may be generated by heating the solids (liquids) in an oven under carefully controlled temperature and flow rate. Permeation and diffusion devices may also be used. The concentration of the individual components generated from these materials (at the selected temperature and flow rate) needs to be verified by duplicate analysis.

7.2 Methanol. Methanol is available from Scott Specialty Gas at useful and certified concentrations.

## 8.0 Sample Collection, Preservation, and Storage

### 8.1 Pretest.

8.1.1 Pretest Information. A screening test is ideal for obtaining proper data that can be used for preparing analytical program files. Information from literature surveys and source personnel are also acceptable. Information about the sampling location and gas stream composition is required to determine the optimum sampling system configuration for sampling formaldehyde, phenol and methanol.

Determine the percent moisture of the flue gas to be analyzed by either EPA Method 4 or by performing a wet bulb/dry bulb measurement. Perform a preliminary traverse of the sample duct or stack and select the sampling point(s). Assess the necessary sampling conditions for the moisture and particulate matter conditions.

Acquire an initial spectrum and determine the proper operational pathlength of the instrument.

8.2 Leak-Check. Measure the leak-rate through the entire sampling system up through the gas distribution manifold. Measure the leak rate of the FTIR system (including the gas cell) before obtaining a background. Use the cell evacuation pump to pull a vacuum on the FTIR cell and system up to the gas distribution manifold. Isolate the cell and system by closing the pump valve. Use the cell pressure gauge to determine leak-rate for a period of time required to obtain one spectrum. The leak volume must be less than 4% of the FTIR cell volume.

8.3 Background Spectrum. Evacuate the gas cell to 5 mmHg. Fill to ambient pressure with dry nitrogen gas and verify that no significant amounts of absorbing species (for example water vapor and CO<sub>2</sub>) have entered the cell. Collect a background spectrum. The signal averaging period of the background spectrum will be at least as long as the averaging period for the sample spectra. The background spectrum will be assigned a unique file name. Two copies of the background interferogram and processed background will be stored on separate computer media.

8.4 Pre-Test Calibration Transfer Standard. Evacuate the gas cell to at least 5 mmHg absolute pressure. Fill FTIR cell to atmospheric pressure with the CTS gas and acquire spectrum.

8.5 Grab Samples. Evacuate the absorbance cell to at least 5mmHg absolute pressure before taking first sample. Fill the cell with flue gas to ambient pressure and record the infrared spectrum, then evacuate the cell until no further evidence of absorption is evident. Repeat this procedure for a sufficient period to collect a representative number of samples (at least 6 separate samples over a 1 hour period).

8.6 Continuous Sampling. Purge the FTIR cell with flue gas for a period of time to equilibrate the stack gas with the sampling/analytical system. The number of spectra (samples) taken is a function of cell volume and sample flow rate through the cell as measured by a calibrated rotameter. The pressure of the FTIR cell should be monitored during spectral acquisition. A sample of gas is isolated by discontinuing the gas cell purge. An infrared spectrum of the captive gas is recorded, and stored to the appropriate computer media. After spectral acquisition, the gas flow is allowed to purge the cell for a time which equals three cell volumes before acquiring the next spectrum. This requires exact knowledge of sample gas flow rate through the FTIR gas cell.

Instrument integration time, sample flow rate, total number of spectra collected, and the total sampling time will be established before testing begins to ensure that a representative sample is obtained. Representative sampling requires that: (1) spectra are recorded of 8-12 unique sample volumes, and (2) the time interval between spectra is consistent with the sampling time resolution required by the administrator.

8.7 Sampling QA, Data Storage and Reporting. Sample integration times should be sufficient to achieve the required signal-to-noise ratios, and all sample spectra should have unique file names. Two copies of sample interferograms and processed spectra will be stored on separate computer media. For each sample spectrum the analyst must document the sampling conditions, the sampling time (while the cell was being filled), the time the spectrum was recorded, the instrumental conditions (path length, temperature, pressure, resolution, integration time), and the spectral file name. A hard copy of these data sheets must be kept available.

8.8 Signal Transmittance. While sampling the analyst must monitor the signal transmittance through

the instrumental system. If signal transmittance (relative to the background) drops below 95 percent in any spectral region where the sample does not absorb infrared energy, then a new background spectrum must be obtained.

8.9 Post-test CTS. After the sampling run completion, record the CTS spectrum.

8.10 Post-test QA. The sample spectra should be inspected immediately after the run to verify that the gas matrix composition was close to the assumed gas matrix, and the sampling and instrumental parameters were appropriate for the conditions encountered. The pre- and post-test CTS spectra should agree within  $\pm 5\%$ .

## 9.0 Quality Control

9.1 Analyte Spiking. Analyte spiking is used to verify the validity of the sampling system for the compounds of interest. In this procedure, analytes are dynamically spiked into the gas stream at a point immediately before the secondary particulate filter.

9.1.1 Spike Materials. Introduce the formaldehyde, phenol, methanol spike compound(s) at a point as close to the probe tip as possible. Introduce the spike gas at a constant flow rate so as to constitute no more than 10% of the total sample flow. Measure the flow rate of the spike with a mass flow meter or equivalent flow device calibrated over the proper range and conditions of use. Determine the total flow to spike flow ratio using appropriate measurement techniques, or use a tracer compound included in the spike gas calibration standard. The tracer must be inert to the sampling system components, not contained in the effluent gas, and readily detected by the analytical instrumentation. Sulfur hexafluoride ( $\text{SF}_6$ ) has been used successfully in the past (Reference 4).

9.2 Procedure. Determine the response time by continuously monitoring effluent until spike is equilibrated within the sampling/analytical system. Allow flue gas to purge through entire sampling system for a period of twice the system response time. Adjust the spike flow rate to approximately 10% of the total flow by metering spike gas through a calibrated flowmeter. Allow spike flow to equilibrate within the sampling system before analyzing first spike samples. A minimum of two consecutive spikes are required. Duplicate analyses of the spiked samples should fall within  $\pm 5\%$  of their mean value. Determine the total flow/spike flow ratio by measuring both the total flow and spike flow rate, or by calculating the dilution ratio from the tracer concentration on a direct and diluted basis.

9.3 Bias. Determine the difference between the observed spike value and the expected response (i.e. the equivalent concentration of the spiked material plus the analyte concentration adjusted for spike dilution). Bias is defined by EPA Method 301 (Section 6.3.1 of 10/91 version) as:

$$B = S_m - M_n - CS \quad (2)$$

Where:

- B = Bias at spike level
- $S_m$  = Mean concentration of the analyte spiked samples
- $M_n$  = Mean concentration of the unspiked samples
- CS = Expected concentration of the spiked samples

## 10.0 Calibration and Standardization

10.1 Calibration transfer standards (CTS). Protocol 1 gases or NIST traceable standards, with a minimum accuracy of  $\pm 2\%$ . For other requirements of the CTS, see the *FTIR Protocol*.

10.2 Noise Ratio. The noise ratio must be less than the minimum acceptable measurement uncertainty in the analytical regions to be used for measuring formaldehyde and phenol.

10.3 Absorbance Pathlength. Verify the absorbance path length by comparing CTS spectra to reference spectra of the calibration gas(es).

10.4 Instrument Resolution. Measure the line width of appropriate CTS band(s) to verify instrumental resolution.

10.5 Apodization Function. Choose appropriate apodization function. Determine any appropriate mathematical transformations that are required to correct instrumental errors by measuring the CTS. Any mathematical transformations must be documented and reproducible.

## 11.0 Analytical Procedure

A full description of the analytical procedure may be found in the *FTIR Protocol*.

#### 12.0 *Data Analysis and Calculations*

Data analysis is performed using appropriate reference spectra whose concentrations can be verified using CTS spectra. Various analytical programs are available to relate sample absorbance to a concentration standard. Calculated concentrations should be verified by analyzing spectral baselines after mathematically subtracting scaled reference spectra from the sample spectra. A full description of the data analysis and calculations may be found in the *FTIR Protocol*.

#### 13.0 *Method Performance*

A full description of the method performance may be found in the *FTIR Protocol*.

#### 14.0 *Pollution Prevention*

This is a gas phase measurement. Gas is extracted from the source, analyzed by the instrumentation, and discharged through the instrument vent.

#### 15.0 *Waste Management*

Laboratory standards prepared from the formaldehyde and phenol are handled as per the instructions enclosed with the materials safety data sheets.

#### 16.0 *References*

1. "Method 301 - Field Validation of Pollutant Measurement Methods from Various Waste Media," *Federal Register*, 57(10), 988-62002, December 29 1992.

2. "Computer-Assisted Quantitative Infrared Spectroscopy," Gregory L. McClure (ed.), *ASTM Special Publication 934* (ASTM), 1987.

3. "Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Mixtures," *Applied Spectroscopy*, 39(10), 73-84, 1985.

4. "Field Validation Test Using Fourier Transform Infrared (FTIR) Spectrometry To Measure Formaldehyde, Phenol and Methanol at a Wool Fiberglass Production Facility." Draft. U.S. Environmental Protection Agency Report. Entropy. Contract #68D20163, I-32.

5. Kinner, L.L., Geyer, T.G., Plummer, G.W., Dunder, T.A., Entropy, Inc. "Application of FTIR as a Continuous Emission Monitoring System." Presentation at 1994 International Incineration Conference, Houston, Tx. May 10, 1994.